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On The Higher Oxides of Zinc and Cadmium

by

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A Thesis Submitted for the Degree of
MASTER OF PHILOSOPHY

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The Higher Oxides of Zinc and Cadmium.

On looking up the peroxide of zinc in the literature considerable uncertainty as to its existence was found. Ladenburg, in his "Handwörterbuch der Anorganischen Chemie", claims that ZnO is the only compound of zinc and oxygen. Dammer mentions no peroxide in his "Handbuch der Anorganischen Chemie", Abegg, in his Handbuch der Anorganischen Chemie", says that a peroxide of zinc seems to exist, and briefly discusses the subject.

A like uncertainty as to the existence of a peroxide of cadmium was found. Dammer makes no mention of a peroxide in his handbook, nor does Ladenburg. Fehling, in "Neues Handwörterbuch der Chemie" states that only one oxidation stage, CdO, is known with certainty. Abegg mentions an impure compound containing cadmium in its higher oxidation stages.

The question of the existence of these peroxides was first investigated by Thenard ("Ann. de chemie et de physique" (2) 9,55,1818.) who claimed that they existed, and later by Haas ("Berichte der Deutschen Chemischen Gesellschaft", 17, 1884, pp. 2250 ff.) who reached the same conclusion. De Forcrand, "Comptes rendus", 134, 601, 1902.) described a whole series of peroxides of zinc with and without water content; Zn_4O_7;Zn_3O_5; and among them also ZnO_2. Kuriloff ("Comptes rendus", 137,618, 1903.) however, claims that they are mixtures of ZnO and ZnO_2.

An account of the work of K.Haas was published in the "Berichte der Deutschen Chemischen Gesellschaft" of 1884,

volume 17, pp. 2249 ff. In this article he gives a brief account of Thenard's method of preparing the peroxides under discussion, which was essentially the following: Method A; hydrated ZnO was dissolved in an HCL solution of H_2O_2 and then precipitated with NaOH or KOH. Method B; he also brought together gelatinous hydrated ZnO and a water solution of H_2O_2. In each case the substances and vessels were kept as cool as possible. He obtained a white gelatinous mass which gave off oxygen on warming, and in dilute acids formed a zinc salt, and H_2O_2. He concluded that the hyperoxidation was incomplete.

Haas, in his investigation, modified Thenard's method somewhat. He treated a solution of a pure zinc salt with a 3% water solution of H_2O_2, and then precipitated with NH_4OH. He used NH_4OH as the precipitant in order to do away with possible side reactions caused by alkali peroxides that might have formed.

The higher oxide of cadmium he attempted to make in the same way.

The precipitates were washed, then dissolved in dilute acid and analyzed for their oxygen content above that required for the formula MO, where M represents the metal. This excess oxygen will be hereafter referred to as $O_\#$. The amount of MO was also determined. The relation MO: $O_\#$ was calculated, and from it the approximate formula of the compound was deduced.

The following tables show his results:

% relation	Analysis I Method A and about 1 hr. standing of mixture.	Analysis II Like I, but 24 hrs. standing.	Analysis III Method B 2 da. standing.
ZnO $O_{\#}$	89.76 10.24 100.00	89.48 10.52 100.00	88.30 11.70 100.00
O in $ZnO:O_{\#}$	1:0.58	1:0.60	1:0.67
Formulae	$Zn_2O_{3.16}$ or Zn_5O_8	$Zn_2O_{3.20}$ or Zn_5O_8	$Zn_2O_{3.24}$ or Zn_3O_5

% relation	Analysis I	Analysis II	Analysis III	Analysis IV	Analysis V
CdO $O_{\#}$	93.1 6.9 100.0	92.3 7.7 100.0	92.9 7.1 100.0	91.3 8.7 100.0	92.04 7.96 100.00
O in $CdO:O_{\#}$	1:0.59	1:0.66	1:0.60	1:0.76	1:0.68
Formulae	Cd_5O_8	Cd_3O_5	Cd_5O_8	Cd_4O_7	Cd_3O_5

In order to determine if the well known MnO_2 could be prepared by similar methods, Haas attempted its preparation from $MnSO_4$. The excess oxygen was determined iodimetrically. The following table shows his results:

% relation	Analysis I	Analysis II	Analysis III
MnO Excess O, $O_{\#}$	89.5 10.5 100.0	89.8 10.2 100.0	88.0 12.0 100.0
Atomic relation O in $MnO:O_{\#}$	1:0.52	1:0.50	1:0.60
Formulae	Mn_2O_3	Mn_2O_3	Mn_5O_8

From these results he drew the following important conclusions:

Higher oxidation stages of both zinc and cadmium do exist. The surprising fact that the manganese compound also did not have the full oxygen content required by the formula MnO_2, but a smaller amount, almost exactly like those of the zinc and cadmium compounds, may be considered of substantial importance in settling the question of the existence of the peroxides of zinc and cadmium, for manganese by other methods of preparation forms a distinct peroxide.

The oxygen content of the cadmium compound is on the average higher than that of the zinc compound. It is more likely correct to regard these oxides of zinc and cadmium as mixtures of the oxides and the dioxides. The constancy of the analyses even allows the supposition that there are binary combinations of the peroxide and monoxide. The assumptions in the case of the oxidation stages of lead and manganese could be made here, viz.: Pb_3O_4; Mn_3O_4; Pb_2O_3; Mn_2O_3; Mn_4O_7, etc. A proof of the existence of the dioxides is the characteristic ability of the compounds to form H_2O_2 with dilute acids. This is valuable evidence even though we disregard these approximate formulae as those of probably impure substances. These compounds show considerable stability toward water and heat. The assumption of a molecular combination of ZnO and H_2O_2 is rendered very unlikely since a portion on standing 12 hours at 120°C still gave a strong H_2O_2 reaction. A portion of the cadmium compound heated 15 hours at 110°C still had excess oxygen enough to indicate 19% CdO_2.

Under the direction of Professor Kahlenberg, the writer studied the higher oxides of zinc and cadmium with a view to determine if their peroxides could be made by the general method suggested by Haas, and to ascertain if an attempt to form MnO_2 by the method of Haas would give results similar to his.

To the writer's knowledge the single potentials of the compounds so produced have never been measured. Their measurement was therefore included in the scope of this study, for the single potentials would be apt to cast some light upon the question of the ease with which the excess oxygen of the higher oxide is given off.

Methods of Procedure.

The zinc superoxides were prepared by the following means: Zinc sulphate crystals of the highest purity, procured from Merck & Co., were dissolved in cold distilled water. A cold water solution of hydrogen peroxide was added. In some cases this was allowed to stand over night, in other cases NH_4OH was added in slight excess very soon after at the temperature of an ice box (below 10°C.).

The hydrogen peroxide used was of various strengths. Merck's 30% highest purity perhydrol was used; also a 1%, and a 3% solution made from it by dilution with distilled water. The perhydrol was first tested for phosphates and these were found absent.

The precipitate was washed by decantation with cold water, dried on porous plate, and afterward over P_2O_5 in the cold.

The cadmium superoxides were prepared in an entirely

similar manner except that Merck's cadmium chloride was used.

The manganese compound was prepared from $MnSO_4$ of the highest purity in a similar manner. Thirty per cent H_2O_2 and 3% H_2O_2 were used, and the product kept cold.

The precipitates of both zinc superoxides and cadmium superoxides were washed as clean as possible with cold water. However, in the case of the cadmium especially, the oxides showed a decided tendency to become colloidal. The ammonium salts remaining as impurity however, would have no effect on the analysis as conducted, nor on the single potentials of these compounds.

Methods of Analysis.

Zinc oxide was determined by suspending the compound in cold water, dissolving with a minimum quantity of HCL, precipitating with a saturated solution of Na_2CO_3, and finally igniting the $ZnCO_3$ to ZnO. This was done in triplicate in all cases but one, that of the zinc superoxide formed by the use of a 1% H_2O_2 solution.

The excess oxygen was determined by titration with standard .0906 normal $KMnO_4$ in H_2SO_4 solution. The titration was performed in the cold by suspending the compound in cold water, adding H_2SO_4 (5cc) while keeping the beaker in ice water, and titrating under the same conditions.

The excess oxygen in the cadmium compound was determined in the same way. Titrations were usually performed in duplicate with the good check results.

Cadmium oxide was determined by weighing as cadmium sulphate. The compound was placed in a weighed crucible and

treated with dilute H_2SO_4. The water was evaporated off on the water bath, the slight excess of H_2SO_4 was driven off by heating in an air bath as suggested in "Analytical Chemistry" by Treadwell-Hall. This analysis was performed in triplicate in all cases.

To determine the relative stability of the compounds of zinc and cadmium at room temperatures, about 22°C, a portion was allowed to stand in the room for one day in one case, for six days in another, after which an analysis was made.

The oxygen in the manganese compound was determined iodimetrically. The compound was treated with quite concentrated HCL, the chlorine evolved passed into a KI solution, and the iodine liberated titrated with $Na_2S_2O_3$. This gave the excess oxygen content, O_t.

The manganese was determined by Volhard's method, by titration of a hot neutral solution of manganous sulphate with $KMnO_4$. The analyses were duplicated.

The single potentials of these peroxides against normal KCL were determined by Poggendorf's compensation method using the normal calomel electrode. A paste of the consistency of tooth paste was made of normal KCL and the superoxide. This was spread over the surface of a clean Acheson graphite rod, and held in place by means of a clean cloth. This was then dipped into a normal KCL solution forming a half cell. The cell was completed by the use of a normal calomel electrode. A dry cell was used as the source of current. It was balanced with a standard Weston cell (E.M.F.=1.01825). A 1000 ohm resistance box, reading to 10 ohms, was used, and an ordinary

portable galvanometer served as the zero instrument.

Experimental Results.

Zinc superoxides:

No.	% ZnO	% $O_{\#}$	% ZnO plus % $O_{\#}$ (total %)	$\frac{\% \text{ ZnO}}{\text{Total}}$ %	$\frac{\% \text{ O}_{\#}}{\text{Total}}$ %	No. of atoms of $O_{\#}$ per ZnO	Approximate formula
1	68.58	9.41	77.99	87.93	12.04		$Zn_{10}O_{16}$
2	68.57	9.35	77.92	88.00	12.00		$Zn_{10}O_{16}$
3	68.12	9.16	77.28	88.15	11.85	.5997	$Zn_{10}O_{16}$
4	70.33	9.66	79.99	87.92	12.08		$Zn_{10}O_{16}$
5	74.85	8.96	83.81	89.31	10.69	.5339	$Zn_{10}O_{15}$
6	75.83	9.67	85.50	88.69	11.31	.5698	$Zn_{10}O_{16}$
7	76.74	9.19	85.93	89.30	10.70	.53[illegible]	$Zn_{10}O_{15}$

Cadmium superoxides:

No.	% CdO	% $O_{\#}$	% CdO plus % $O_{\#}$ (total %)	$\frac{\% \text{ CdO}}{\text{Total}}$ %	$\frac{\% \text{ O}_{\#}}{\text{Total}}$ %	No. of atoms of $O_{\#}$ per CdO	Approximate formula
1	70.81	2.45	73.26	96.65	3.34		$Cd_{10}O_{13}$
2	70.71	2.45	73.16	96.65	3.34		$Cd_{10}O_{13}$
3	70.44	2.40	72.84	96.70	3.29	.2730	$Cd_{10}O_{13}$
4	71.24	2.42	73.66	96.71	3.29		$Cd_{10}O_{13}$
5	77.77	3.46	81.23	95.74	4.26	.3567	$Cd_{10}O_{14}$
6	76.56	6.59	83.15	92.07	7.93	.6911	$Cd_{10}O_{17}$
7	76.59	6.47	83.06	92.21	7.79	.6780	$Cd_{10}O_{17}$

Manganese superoxides:

No.	% Mn	% MnO calculated	% O#	% MnO plus % O# (total %)	% MnO / Total %	% O# / Total %	No. of atoms of O# per MnO	Approximate formula
1	41.88	54.08	10.22	64.30	84.10	15.90	.6657	$Mn_{10}O_{16}$
2	46.55	60.11	14.90	75.01	80.14	19.86	1.073	MnO_2

Single potentials against normal KCL solution:

Super oxide	Bridge reading (ohms)	Weston against Dry-cell (ohms)	E.M.F. of Weston (volts)	Potential of calomel electrode (volts)	Potential of material. (Mean)
Cd no.1	50 50	647	1.01825	+.56	+.639
Cd No.6	40 36	640	"	"	+.620
Cd no.7	43 20	640	"	"	+.610
Zn no.1	60 50	647	"	"	+.647
Zn no.6	45 40	640	"	"	+.628
Zn no.7	30 40	640	"	"	+.615
Mn no.1	50 45	640	"	"	+.636
Mn no.2	38 40	640	"	"	+.622

Single potentials of PbO_2:

1. Against .5 normal H_2SO_4 = 1.5305 volts.

2. Against normal KCL = 1.100 volts

Mangenese superoxides:

No.	% Mn	% MnO calculated	% O#	% MnO plus % O# (total %)	% MnO / Total %	% O# / Total %	No. of atoms of O# per MnO	
1	41.88	54.08	10.22	64.30	84.10	15.90	.6657	Mn
2	46.55	60.11	14.90	75.01	80.14	19.86	1.073	Mn

Single potentials against normal KCL solution:

Super oxide	Bridge reading (ohms)	Weston against Dry-cell (ohms)	E.M.F. of Weston (volts)	Potential of calomel electrode (volts)	Potential material. (Mean)
Cd no.1	50 50	647	1.01825	+.56	+.639
Cd No.6	40 36	640	"	"	+.620
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Mn no.1	50 45	640	"	"	+.636
Mn no.2	38 40	640	"	=	+.622

Single potentials of PbO_2:

1. Against .5 normal H_2SO_4 = 1.5305 volts.
2. Against normal KCL = 1.100 volts

Discussion of the Experimental Results.

Zinc superoxide.

Numbers 1 to 4 inclusive were prepared by the use of 30% hydrogen peroxide. Number 1 was kept cold, Number 2 was exposed to room temperature about one day; Number 3 was exposed to room temperature for about six days. Numbers 1 to 3 inclusive were dried over $CaCl_2$ for about six days. Number 4 was dried over $CaCl_2$ for six days and then over P_2O_5 an equal period. Numbers 1 and 4 were kept cold. It will be observed that the analyses gave fairly constant results, the formulae in each case being approximately $Zn_{10}O_{16}$. Number 5 was made with 3% H_2O_2 and had been standing exposed to room temperature in a closed weighing bottle for about seven months, including the summer months. It had a somewhat lower oxygen content than 1 to 4 inclusive. Number 6 was prepared by the use of 3% H_2O_2, and kept cool. This was the only case in which results were obtained that did not check as closely as in the other cases. However, it will be seen that here also a higher oxide was obtained, the percentage of excess oxygen being between that in Number 3 and that in Number 5. Number 7 was prepared by the use of a 1% H_2O_2 solution, and kept cool. Its content of excess oxygen is about the same as that in number 5.

From these results it would appear that in the case of zinc a slightly higher superoxide is obtained by the use of 30% H_2O_2 than by the use of weaker solutions. It would also appear that on standing at room temperature there is a very slight loss of excess oxygen. All these compounds were pure white.

Discussion of the Experimental Results.

Zinc superoxide.

Numbers 1 to 4 inclusive were prepared by the use of 30%
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bottle for about seven months, including the [illegible]
had a somewhat lower oxygen content than [illegible]
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seen that here also a higher oxide was [illegible] of excess
of excess oxygen being between [illegible]
Number 5. Number 7 was prepared [illegible]
solution, and kept cool. Its [illegible]
the same as that in number [illegible]

From these results [illegible] e of 30% H_2O_2; Number 2
a slightly higher super[illegible] pounds were medium brown in
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excess oxygen. [illegible]

Conclusions.

The results of this investigation substantially confirm the findings of R. Haas.

Higher oxidation stages of cadmium and zinc do exist. Dilute H_2O_2 solutions are better adapted to the preparation of cadmium superoxides than concentrated solutions. Concentrated solutions of H_2O_2 are slightly better for the formation of the zinc superoxides.

Pure peroxides of zinc and cadmium of the general formula MO_2 can not be prepared by this method. These compounds may be mixtures of MO and MO_2 altho the author does not think so. They react with HCL forming H_2O_2 which could be titrated with $KMnO_4$, showing that peroxides of zinc and cadmium do exist.

With 3% H_2O_2, however, the writer was able to get MnO_2, but not with 30% H_2O_2.

In the case of the single potentials it is to be noted that the potential of PbO_2 is far greater than that of any of the other peroxides. When we compare the single potentials of cadmium, zinc, and manganese with one another, we note that their values are not materially different as to general order of magnitude. In fact the differences noted are such that one would hardly be warranted in drawing any further conclusions especially when the experimental difficulties in making such measurements are considered.

Approved

Feb. 15/1918.

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